Chemical Engineering Journal 287 (2016) 130–138

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Experimental studies and modelling of a simplified CIP system using ozone and linear alkylbenzenesulfonate

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HIGHLIGHTS

- Degradation of alkylbenzenesulfonate by ozone in a cleaning device has been modeled.
- A new model considering ozone and surfactant has been synthesised and tested.
- The detergency with surfactant and ozone was similar to experiments without ozone.
- Ozone reduces the surfactant toxicity without affecting the washing effectiveness.

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 6 October 2015
Accepted 7 November 2015
Available online 1 December 2015

Keywords:
Ozone
Alkylbenzenesulfonate
Kinetic ozonation model
Anionic surfactant
CIP system

ABSTRACT

The degradation of linear alkylbenzenesulfonate by ozone in a simplified CIP system has been explained considering jointly a first-order kinetic model for the ozone decomposition reaction in aqueous solutions and a first-order kinetic model for the reaction of ozone and homologues of linear alkylbenzenesulfonate (LAS). The kinetic constants found for the homologues of LAS at the same temperature are similar and show good dependence on temperature ($0.960 < r^2 < 0.995$) following the Arrhenius equation, indicating that ozone has similar affinity for the different alkyl chain homologues.

The cleaning of soiled substrate using LAS solutions and ozonated LAS solutions has also been analysed. Under these experimental conditions, the detergency was almost the same without affecting the washing effectiveness. However, a degradation of the surfactant is obtained when ozone is used, reducing the toxicity of the washing solutions. This indicates that LAS could have potential as a surfactant in CIP system with ozone.

1. Introduction

The use of ozone as an alternative to chlorine and other chemical disinfectants in cleaning and disinfection operations has been growing in recent years due to its high biocidal efficacy, absence of chlorine that may form secondary pollutants [1], low running costs, possibility of an initial biodegradation in the effluent sewage [2,3], and the possibility of being generated *in situ* [4]. This technology also unifies the cleaning process with the possibility of biodegradation of surfactants and soils in one production step [5]. Thus, for example, Pascual et al. [4] reviewed the uses of ozone in cleaning in the food industry.

Moreover, the approval of ozone by the U.S. Food and Drug Administration (FDA) for use in food treatment, storage, and processing, together with the environmental legislation in Europe (IPPC Directive 96/61/EC), have increased interest in this technique, given that cleaning and disinfection are responsible for the greatest environmental impacts (water and energy consumption, wastewater, etc.) in many processing plants.

When ozone is used in a cleaning process, it sometimes becomes necessary to use high cleaning times or severe conditions to reach the detergency required. In these cases it might be helpful to introduce surfactants that improve detergency. These should be surfactants initially resistant to the degradation by ozone. Later, after reaching the cleaning requirements, the cleaning conditions could be adjusted (basically temperature and ozone concentration) to degrade the surfactants and soils in an effort to reduce the environmental impact of the cleaning wastewater.

The kinetics and mechanism of the oxidation of surfactants by ozone in aqueous solutions have been studied by several researchers [2,6] and specifically with linear alkylbenzenesulfonate (LAS) by

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http://dx.doi.org/10.1016/j.cej.2015.11.032

Abbreviations

BSF	Bath–Substrate–Flow system
C_{LASi}	concentration of each LAS homologue, Eq. (7) (M)
C_{LASi0}	initial concentration of the LAS homologue considered (M)
C_{O3}	ozone concentrations in the aqueous phase, Eq. (5) (M)
C_{O3}^{*}	ozone concentrations in the liquid–gas interface (M)
C_{O3s}	ozone concentration in the aqueous solutions at the steady-state (M)
CV	coefficient of variation (%)
De	detergency (%)
E_a	activation energy (kcal mol^{-1})
k_D	rate constant of the ozone decomposition in water (s^{-1})
k_i	kinetic constant (L mol^{-1} s^{-1})
k_{i0}	preexponential value (L mol^{-1} s^{-1})
$k_L\,a$	volumetric mass-transfer coefficient through the water phase (s^{-1})
LAS	linear alkylbenzenesulfonate
LAS-C_{10}	LAS homologue (carbon-chain length C_{10})
LAS-C_{11}	LAS homologue (carbon-chain length C_{11})
LAS-C_{12}	LAS homologue (carbon-chain length C_{12})
LAS-C_{13}	LAS homologue (carbon-chain length C_{13})
MBAS	methylene blue active substance
t	time (s)
T	temperature (°C)
TOC	total organic carbon (mg L^{-1})
Total-LAS	sum of the homologues C_{10}, C_{11}, C_{12} and C_{13}
x	conversion (–)

Beltran et al. [7], Ikehata and El-Din [8], and Zsilak et al. [9]. LAS is an anionic surfactant used in household and industrial detergents that merits special attention due to its excellent detersive properties. It is composed of a mixture of homologues and isomers. The length of the alkyl chain is frequently from C_{10} to C_{13}. It has been demonstrated that LAS is readily biodegradable by aerobic processes, but not by anaerobic conditions [10]. Less work has been done to determine the conditions under which the surfactants, and specifically LAS, can provide better performance with ozone. In recent years, the main efforts have been focused on evaluating the properties of the ozonated surfactant solutions, such as the biodegradability of aqueous solutions of LAS [11,12], the time course of the surface tension during ozonation when different surfactants such as LAS or alkylpolyglucosides are used [11,12], the foaming effect on the ozonated solutions of LAS [13] or the addition of enzymes to ozonated aqueous solutions for improving the detersive effect of these solutions [14]. These efforts are oriented towards determining the optimum conditions in industrial cleaning processes where both effects, the ozone effect (as a cleaner and disinfectant) and surfactant effect (as a detersive agent), are necessary.

On the other hand, knowing the reaction between different homologues and ozone has interest due to the different performance that they can show. Different authors have indicated that the toxicity of LAS generally intensifies as the number of carbon atoms in the alkyl chain increases [15,16] and that interfacial properties of the surfactant molecules are correlated with bioconcentration and toxicity of LAS [17]. For example, the C_{10} and C_{11} homologues of LAS can move more quickly to deeper layers of soiling agent than can C_{12} and C_{13} homologues, which require larger amounts of water to be carried deeper [18].

The aim of the present study is to determine the degradation of the different homologues of LAS as a function of the ozone and LAS concentration, temperature, and time reaction. These models could allow us to determine under what conditions the performance of ozone and surfactant could be optimised to attain better cleaning results. Also, this would unify into a single production stage the processes of cleaning and degradation of organic matter present in wastewaters.

2. Materials and methods

2.1. Materials

The anionic surfactant used was linear alkylbenzenesulfonate (LAS), supplied by Cepsa Química (San Roque). LAS is a mixture of homologues and isomers, the characterisation of which was supplied by the manufacture (moisture 54.6%; carbon-chain length C_{10}–C_{13}: 16.6% C_{10}, 32.6% C_{11}, 28.9% C_{12}, 21.9% C_{13}). The concentration of the LAS solutions are expressed in dry weight [19] and the critical micelle concentration (CMC) is 1.018 g/L (37 °C) [20]). The reagents used in the chromatographic analysis were methanol (HPLC-gradient grade) and sodium dodecyl sulphate (SDS) (Panreac).

For the washing tests the substrate used was borosilicate glass beads (3 mm diameter) from Simax (Kavalier, Sázava, Czech Republic). An alimentary fat, pork lard, from "El Pozo", Spain, was used as the soiling agent, stored at 4 °C until used. As soiling agent neat (untreated) and ozonated pork lard were tested. To determine the concentration of the fat, it was stained with the fat-soluble pigment Sudan III (0.02% w/w), so it could be determined spectrophotometrically at 500 nm. To account for the possible degradation of Sudan III by ozone, calibration curves were constructed with both untreated and ozonated pork lard.

2.2. Ozonation device

The ozonation of the surfactant solution and the cleaning process were undertaken in a modified Bath–Substrate–Flow system (Fig. 1). Fig. 1 shows the scheme of the ozonation and cleaning device. This device simulates a cleaning-in-place system and can evaluate the detergency produced on hard surfaces [21–23]. The ozonation device used 500 mL of water or aqueous surfactant solutions and had a jacketed stirred tank, a peristaltic pump (supplying 30 L h^{-1} flow), a packed column (diameter 2.5 cm, height 8.5 cm), a thermostatically controlled bath, a diffuser, a paddle stirrer and a thermometer. It also contained a $O_3 + O_2$ diffuser located at the bottom of reactor. The aqueous solution was extracted from the jacketed stirrer tank by the peristaltic pump, flowed upwards in the column, and finally returned to the tank. The temperature of the jacketed stirrer tank and packed column was kept constant using the thermostatic bath. The ozone generator (Anseros Peripherals COM-AD, Germany) used oxygen to produce the ozone onsite. The ozone concentration in the ozone-oxygen mixture was determined by an ozone analyser (Ozomat GM-6000-PRO, Anseros, Germany). The ozone-oxygen mixture was introduced in the reactor (flow 40 NL h^{-1}, 70 g m^{-3} ozone inlet concentration) by the diffuser located at the bottom of the reactor. The gas leaving the system passed through gas washing flasks filled with a potassium iodide solution, in which the ozone oxidised iodide ions.

2.3. Analysis of ozone in aqueous solutions

The ozone concentration was evaluated using the indigo method [24]. Samples (5 mL) were mixed with 1 mL of indigo